

## **EtO Ambient Air Sampling Procedures Using Canisters with Passive Vacuum Regulators**

The procedure presented is designed for sampling volatile organic compounds (VOCs) in ambient air, based on the collection of whole air samples in SUMMA® treated canisters to final pressures below atmospheric. The samples are then analyzed using EPA Compendium Method TO-15 *Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)*.

### **Sampler Installation**

1. The sampling system consists of two components: a sample canister and a passive vacuum regulator (Veriflow vacuum regulator with gauge and sample inlet probe). The canisters have been cleaned, tested for contamination (blanked) and evacuated, the passive collection assemblies will have been cleaned, tested for contamination (blanked), and calibrated for 24-hour integrated sampling.
2. The complete sampling system must be securely mounted on a support structure which ensures that the sample inlet meets the siting criteria (See QAPP for details <https://www.epa.gov/il/quality-assurance-project-plan> section 2.1.2).
3. For collocated samplers, horizontal spacing should be between 0 and 4 meters, and inlet heights within 1 meter vertically.

## **OPERATING PROCEDURE**

### **A. Equipment and Supplies**

1. 6-liter sample collection canister
2. Veriflow vacuum regulator/gauge/inlet probe (passive collection assembly)
3. Chain of Custody (COC) form

### **B. Sampler and Sample Media Receipt Activities**

#### **Complete Sampling System**

1. Check parts and components to ensure none is damaged.
2. Ensure all fittings are present and in good condition.
3. Prior to sampling keep all sampling system components in a clean area free of contamination.
4. Ensure the canister is not damaged. Confirm that the valve remained in the closed position during transport and that the top plug is secured on the bellows valve inlet fitting.

### **C. Preparing for a Sampling Event**

1. Prepare sample paperwork. On the COC, supply all required information in the “Lab Pre-Sampling” section. Record any pertinent observations in the “Comments” section at the bottom of the form.
2. Remove the plug attached to the bellows valve inlet. Retain the plug in a clean place so that it can be used to reseal the bellows valve inlet after the sampling event.
3. Assemble the complete sampling system.
  - a. Attach the outlet fitting of the Veriflow vacuum controller to the canister bellows valve inlet fitting. *Note: Do not over tighten the fitting nut. When the fitting nut feels snug by*

*hand, another quarter turn should be sufficient to secure the controller inlet to the canister.*

- b. Ensure that the plug at the inlet of the Veriflow remains tight in order to perform a leak check. Perform a leak check by opening and then immediately closing the canister valve. Observe the vacuum reading on the Veriflow gauge. If the vacuum changes by more than 1 in Hg over 5 minutes, ensure that all fittings are tight. If all fittings are tight, then assemble another sampling system using another canister and repeat steps 2 and 3.

#### **D. Sampling and Data Collection**

1. Record the initial collection start time and date in “Setup Date:” in the “Field Setup” section on the COC form. Fully open the canister bellows valve. Observe the pressure (i.e., “Hg vacuum”) indicated on the gauge.
2. After 24 hours, read the gauge and record the remaining pressure left in the can on the COC and record the reading in the “Field Recovery”, “Field Final Can. Press. (“Hg)” blank. If the pressure is zero, note the lack of pressure in the “Comments” section of the form.
3. Close the canister bellows valve fully.
4. Disconnect the canister from Veriflow vacuum controller by unfastening the Veriflow outlet fitting from the canister bellows valve inlet fitting.
5. Replace and secure the retained plug on the canister bellows valve.
6. On the COC, supply all required information in the “Field Recovery” section. Be sure to record any observations that were made during the run period in the “Comments:” section.

## Technical Note on Ethylene Oxide analysis by EPA TO-15 Method

Ethylene oxide (EtO) is an emerging pollutant that is quantified using the existing EPA TO-15<sup>1</sup> method with some modifications. The typical method setup scans for selected fragment ions (also known as selected ion monitoring mode or SIM) instead of a full spectrum scan in order to increase the analytical sensitivity and efficiency. However, SIM introduces uncertainties and limitations due to decreased collected full scan spectra information. Using SIM, another compound with common fragment ions (primary and secondary) and similar retention time windows as the target compound could be an interferant to the target compound, biasing quantitation results.

The EPA contract laboratory has confirmed that trans-2-butene co-elutes with EtO, creating an interference. The monitoring ions the contract laboratory selected for EtO before October 2018 were 15, 29 and 43; EtO was quantitated based on ion 29. Upon discovery of the interferant, the contract laboratory modified their analytical method to include additional unique confirmatory fragment ions to aid the identification and quantification processes. The modified method is scanning for ions 15, 29, 44, and 41 as well as ion unique to trans-2-butene (ion 56). For quantitation, the most intense ion 29 from EtO is used as the base quantitation peak (ions 15 and 44 as qualifying ions). Although the second most abundant ion (44) is in EtO and absent from trans-2-butene, the lower sensitivity and variable background issues (eg. carbon dioxide) associated with ion 44 make it less desirable for quantitation of EtO. The contract laboratory has analyzed standards that include EtO and the interferant trans-2-butene and is able to accurately identify and quantitate each compound using the modified method.

See Figures 1 and 2 for example chromatograms and spectra for samples analyzed by the modified method (scanning for ions, 15, 29, 44, 41 and 56) illustrating a sample with and without the presence of trans-2-butene, respectively.

In Figure 1, a prepared standard including the mixture of trans-2-butene and EtO at 0.25ppbv (individual concentration) was analyzed by SIM scanning for ions 15, 29, 44 as well as 41 and 56. At the target retention time window for EtO and trans-2-butene, the sample spectrum captured strong signals for ions 15, 29 and 44 as well as ions 41 and 56, which indicates and confirms the presence of trans-2-butene. In addition, the chromatograms for ions 41 and 56 were further examined to confirm that the first peak is correctly identified as trans-2-butene, and the second peak detected at 12.466 minutes is determined to be EtO and quantitated as such (determined concentration circled in figure as 0.24ppbv).

In Figure 2, an ambient sample collected at Willowbrook Village Hall on 19<sup>th</sup> November, 2018 was analyzed by SIM scanning for ions 15, 29, 44 as well as 41 and 56. At the target retention time window for EtO and trans-2-butene (established by standards), the sample spectrum captured strong signals for ions 15, 29 and 44 but minimal to no signal for ions 41 and 56, which indicates the absence of trans-2-butene. Also, by comparing to the EtO reference spectrum recorded from an EtO standard analyzed by the contract laboratory, the relative ratios of the sample for ions 15, 29 and 44 match closely with the established reference ratios. Coupled with the retention time

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<sup>1</sup> [https://www.epa.gov/sites/production/files/2015-07/documents/epa-to-15\\_0.pdf](https://www.epa.gov/sites/production/files/2015-07/documents/epa-to-15_0.pdf)

window, the peak detected at 12.395 minutes is determined to be solely EtO and quantitated as such (determined concentration circled in figure as 3.38ppbv).

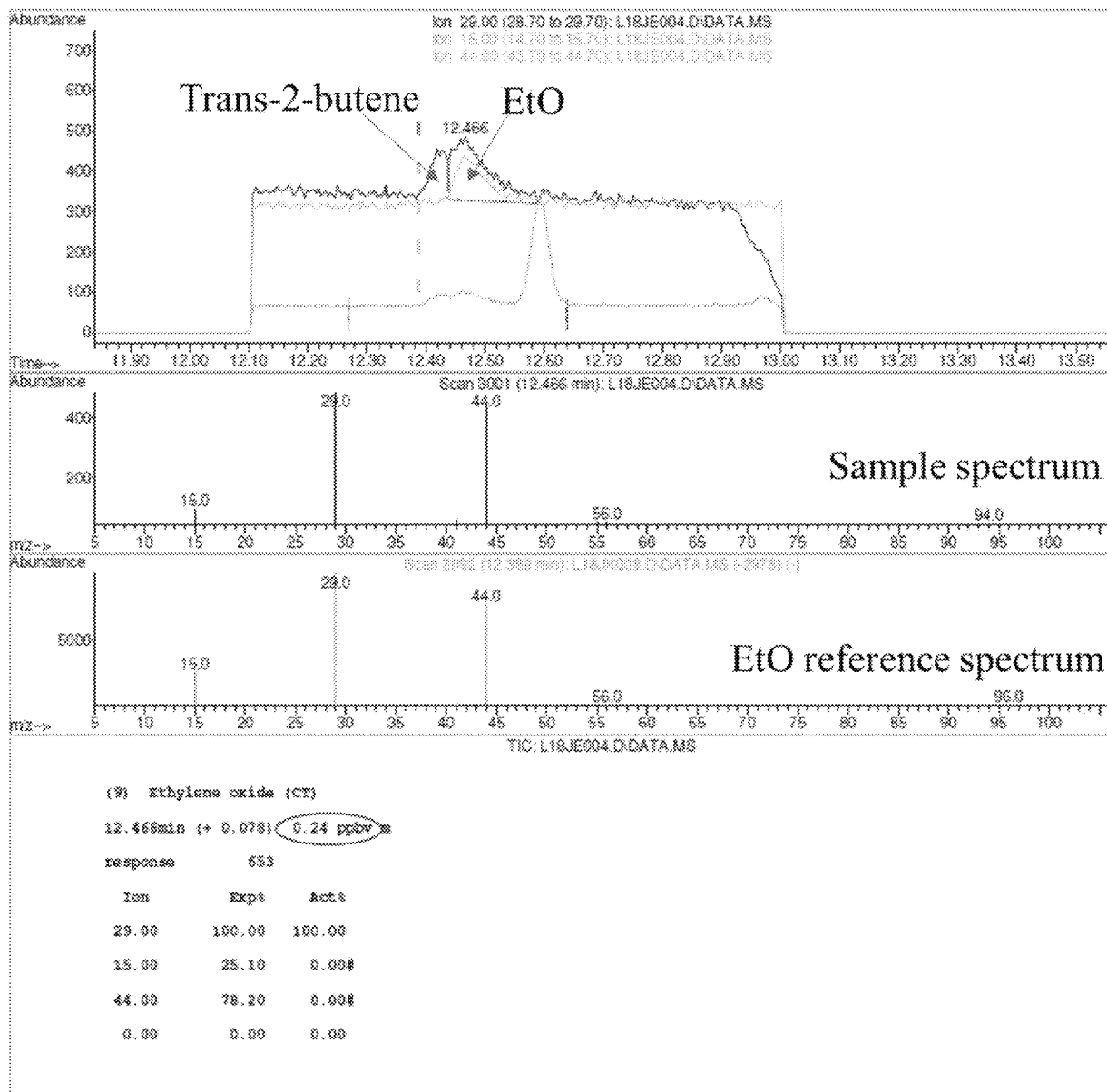


Figure 1. Example chromatogram and spectrum for a mixture standard (including both trans-2-butene and EtO) analyzed for EtO by the modified TO-15 method.

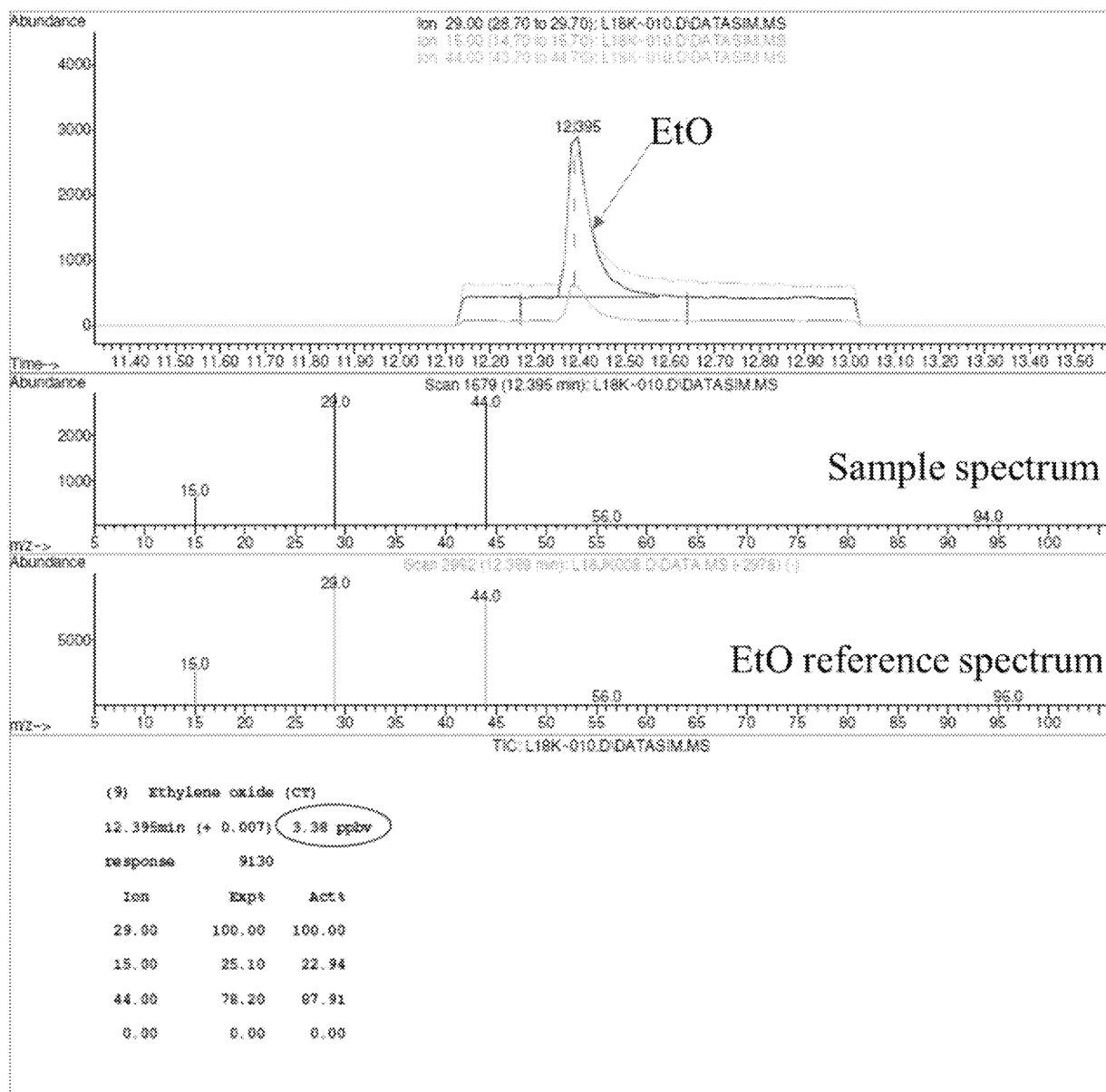


Figure 2. Example chromatogram and spectrum for a sample (collected at Willowbrook Village Hall on November 19<sup>th</sup>) analyzed for EtO by the modified TO-15 method.

## Quality Control and Data Validation Requirements for Ethylene Oxide Sampling and TO-15 Analysis

### Calibration and Calibration Check Frequency Requirements for Standards and Critical Instruments

Instrument or Standard	Area of Use	Required Calibration Check <sup>a</sup> Frequency and Tolerance	Required Calibration <sup>b</sup> Frequency
Balances	Laboratory – Weighing standard materials, calibration of pipettes, determining mass loss for microwave metals digestion, weighing PAHs sorbent resin (XAD-2)	Each day of use with certified calibration check weights bracketing the balance load; Must be within manufacturer-specified tolerance covering the range of use	Initially, annually, and when calibration checks demonstrate an out of tolerance condition
Certified Weights	Laboratory – Calibration verification of balances	Check not required.	Annual certification by accredited metrology laboratory; Must be within manufacturer-specified tolerance
Mechanical Pipettes	Laboratory – Dispensing liquid volumes	Minimally quarterly, recommended monthly, by weighing delivered volumes of deionized water bracketing those dispensed; Must be within manufacturer-specified tolerance covering the range of use	Initially and when calibration checks demonstrate an out of tolerance condition
Bottletop Dispensers	Laboratory – Dispensing critical liquid volumes	Each day of use by delivery into a To Contain (TC) graduated cylinder Must be within $\pm 5\%$	When delivery volumes are set and when calibration checks fail criteria
Thermometers – Laboratory	Laboratory – Temperature monitoring of water baths, metals digestion, refrigerated storage units, canister cleaning ovens, and water for pipette calibration	Check not required.	Annual at temperature range of use or at not-to-exceed temperature – Correction factors applied to match certified standard
Thermometers – Meteorological	Field – Recording environmental conditions during sample collection	Minimally quarterly, monthly recommended  Must be within $\pm 0.5^{\circ}\text{C}$ of certified standard at working temperature	Initially and when calibration checks indicate readings out of tolerance
Barometers	Field – Recording environmental conditions during sample collection  Laboratory – Recording environmental conditions during instrument calibration	Minimally quarterly, monthly recommended  Must be within $\pm 10$ mm Hg of certified standard at typical barometric pressure	Initially and when calibration checks indicate readings out of tolerance
Flow Transfer Standards	Field – Critical flow orifices and volumetric flow meters	Check not required.	Annual; Must be within manufacturer-specified

<b>Instrument or Standard</b>	<b>Area of Use</b>	<b>Required Calibration Check <sup>a</sup> Frequency and Tolerance</b>	<b>Required Calibration <sup>b</sup> Frequency</b>
	for calibrating and verifying sampling unit flows  Built-in thermometers and barometers must be calibrated		tolerance and cover the range of use
Pressure Gauges or Transducers	Field and Laboratory – Measure canister pressure/vacuum before and after collection, measure final canister vacuum following cleaning	Annual. Must be within 0.5 psi or manufacturer-specified tolerance and cover the range of use	Initially and when calibration checks show out of tolerance. Must cover the range of use
Flow Controllers and Meters – Laboratory	Laboratory – Mass flow controllers (MFCs), flow rotameters, or similar devices for measuring/metering gas flow rates for critical measurements (standard gas mixing)	Minimally quarterly, monthly recommended  Flow within $\pm 2\%$ of certified standards	Initially and when calibration checks demonstrate flows are out of tolerance
VOCs Sampling Units	Field – Collection of VOCs in canisters  Flow control (such as MFC)  Pressure gauge/transducer	If performed, minimally quarterly, for flow control, annually for pressure gauge/transducer  Flow control (check is optional) within $\pm 10\%$ of certified flow  If needed for critical measurements (canister starting/ending pressure), pressure gauge/transducer within $\pm 0.5$ pounds per square inch (psi) of certified standard	Flow control - Initially and when components affecting flow are adjusted or replaced, or when calibration checks demonstrate flows are out of tolerance  Pressure gauges/transducers – initially and when calibration checks demonstrate flows are out of tolerance
GC/MS for VOCs analysis	Laboratory – Analysis of VOCs from stainless steel canisters	Refer to Table 4.2-3	Initially, following failed continuing calibration verification (CCV) check, following failed bromofluorobenzene (BFB) tune check, or when changes/maintenance to the instrument affect calibration response

**Summary of Quality Control Parameters for NATTS VOCs Analysis{ TC "Table 4.2-3.  
Summary of Quality Control Parameters for NATTS VOCs Analysis" \FD \ "1" }**

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Instrument Blank (IB)	Analysis of swept carrier gas through the preconcentrator to demonstrate the instrument is sufficiently clean to begin analysis	Prior to ICAL and daily beginning CCV	Each target VOC's concentration < 3x MDL or 0.2 ppb, whichever is lower
BFB Tune Check	50 ng injection of BFB for tune verification of quadrupole MS detector	Prior to initial calibration and every 24 hours of analysis thereafter	Abundance criteria listed in Table 4.2-2
Initial Calibration (ICAL)	Analysis of a minimum of five calibration levels covering approximately 0.1 to 5 ppb	Initially, following failed BFB tune check, failed CCV, or when changes/maintenance to the instrument affect calibration response	Average RRF $\leq$ 30% RSD and each calibration level must be within $\pm$ 30% of nominal  For quadratic or linear curves, $r \geq 0.995$ , each calibration level must be within $\pm$ 30% of nominal
Secondary Source Calibration Verification (SSCV)	Analysis of a secondary source standard at the mid-range of the calibration curve to verify ICAL accuracy	Immediately after each ICAL	Recovery within $\pm$ 30% of nominal or RRF within $\pm$ 30% of the mean ICAL RRF
Continuing Calibration Verification (CCV)	Analysis of a known standard at the mid-range of the calibration curve to verify ongoing instrument calibration	Following each daily BFB tune check and every 24 hours of analysis; recommended after each ten sample injections and to conclude each sequence	Recovery within $\pm$ 30% of nominal or RRF within $\pm$ 30% of the mean ICAL RRF
Canister Cleaning Batch Blank	A canister selected for analysis from a given batch of clean canisters to ensure acceptable background levels in the batch of cleaned canisters	One canister from each batch of cleaned canisters – Canister chosen must represent no more than 10 total canisters.	Each target VOC's concentration < 3x MDL or 0.2 ppb, whichever is lower (All Tier I Core analytes must meet this criterion)
Internal Standards (IS)	Deuterated or not naturally occurring compounds co-analyzed with samples to monitor instrument response and assess matrix effects	Added to all calibration standards, QC samples, and field-collected samples	Area response for each IS compound within $\pm$ 40% of the average response of the ICAL
Preconcentrator Leak Check	Pressurizing or evacuating the canister connection to verify as leak-free	Each standard and sample canister connected to the instrument	< 0.2 psi change/minute or manufacturer recommendations
Method Blank (MB)	Canister filled with clean diluent gas	One with every analysis batch of 20 or fewer field-collected samples	Each target VOC's concentration < 3x MDL or 0.2 ppb, whichever is lower
Laboratory Control Sample (LCS)	Canister spiked with known amount of target analyte at approximately the lower third of the calibration curve	(Recommended) One with every analysis batch of 20 or fewer field-collected samples	Each target VOC's recovery must be 70 to 130% of its nominal spiked amount
Duplicate Sample	Field sample collected through the same inlet probe as the primary sample	10% of primary samples for sites performing duplicate sample	Precision $\leq$ 25% RPD of primary sample for



Parameter	Description and Details	Required Frequency	Acceptance Criteria
		collection (as prescribed in workplan)	concentrations $\geq 5x$ MDL
Collocated Sample	Field sample collected through a separate inlet probe from the primary sample	10% of primary samples for sites performing collocated sample collection (as prescribed in workplan)	Precision $\leq 25\%$ RPD of primary sample for concentrations $\geq 5x$ MDL
Replicate Analysis	Replicate analysis of a field-collected sample (chosen by analyst)	Once with every analysis sequence (as prescribed in workplan)	Precision $\leq 25\%$ RPD for target VOCs with concentrations $\geq 5x$ MDL
Retention Time (RT)	RT of each target compound and internal standard	All qualitatively identified compounds and internal standards	Target VOCs within $\pm 0.06$ RRT units of mean ICAL RRT  IS compounds within $\pm 0.33$ minutes of the mean ICAL RT

## VOCs via EPA Compendium Method TO-15 – Frequencies and Acceptance Criteria

The following table is a distillation of the general quality control guidance and requirements in Section 3 and the individual methods described in Section 4 of the NATTS Technical Assistance Document. More information on each data validation parameter can be located within the text identified in the reference column. Each parameter is assigned a category of importance. The categories in order of decreasing importance are:

1. Critical – Criteria must be met for reported results to be valid – Samples for which these criteria are not met are invalidated.
2. MQO – Required NATTS Measurement Quality Objective which must be attained – Failure to meet these criteria does not necessarily invalidate data, but may compromise data and result in exclusion from trends analysis.
3. Operational – Failure to meet criteria does not invalidate reported results; the results are compromised and on a case-by-case basis may require qualification – refer to Section 3.3.1.3.15 for the list of AQS qualifiers
4. Practical – Failure to meet criteria does not invalidate reported results; results may be compromised but do not require qualification.

{ TC "7.1 VOCs via EPA Compendium Method TO-15" \f C \l "2" }

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
<i>Field Readiness Checks and Collection Activities</i>				
Canister Cleaning Batch Blank	Minimally one canister selected for analysis from a given batch of clean canisters to ensure acceptable background levels in the batch of cleaned canisters - must represent no more than 10 canisters	Each target VOC's concentration < 3x MDL or 0.2 ppb, whichever is lower	Section 4.2.6.2.4 TO-15 Section 8.4.1.6	Critical
Canister Viability	All canisters	Canister must be used within 30 days from final evacuation	Section 4.2.6.2 TO-15 Section 1.3	Operational
Sampling Unit Clock/Timer Check	Verified with each sample collection event	Clock/timer accurate to ±5 minute of reference for digital timers, ±15 minutes for mechanical timers, set to local standard time  Sample collection period verified to be midnight to midnight	Section 4.2.5.3 and Table 3.3-1	Operational
Canister Starting Pressure Determination	Each canister prior to collection of a field sample or preparation of a calibration standard or laboratory QC sample	Vacuum > 28" Hg as determined with calibrated pressure gauge or transducer	Section 4.2.5.2.1	Critical
Sample Setup Leak Check	Each canister prior to collection - draw vacuum on canister connection	Leak rate must be < 0.2 psi over 5 minutes	Section 4.2.5.2.1	Critical

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Sampling Frequency	One sample every six days according to the EPA National Monitoring Schedule	Sample must be valid or a make-up sample should be scheduled (refer to Section 2.1.2.1)	Section 4.2.5.3	Critical and MQO
Sampling Period	All field-collected samples	1380-1500 minutes (24 ± 1 hr) starting and ending at midnight	Section 4.2.5.3	Critical and MQO
Pre-Sample Collection Purge	Each sampling event	Minimum of ten air changes just prior to sample collection	Section 4.2.5.4	Practical
Field-collected Sample Final Pressure	All field-collected samples	Must be determined with a calibrated pressure gauge or transducer per agency quality system specification	Section 4.2.5.2.4	Operational
<b>Sample Receipt</b>				
Chain-of-custody	All field-collected samples including field QC samples	Each canister must be uniquely identified and accompanied by a valid and legible COC with complete sample documentation	Sections 3.3.1.3.7 and 4.2.5.2.4	Critical
Sample Holding Time	All field-collected samples, laboratory QC samples, and standards	Analysis within 30 days of end of collection (field-collected samples) or preparation (QC samples or standards)	Section 4.2.1 TO-15 Sections 1.3, 2.3, and 9.2.8.1	Operational
Canister Receipt Pressure Check	All field-collected samples upon receipt at the laboratory – measured with calibrated pressure gauge or transducer	Pressure change of $\leq 0.5$ psi from the final pressure at retrieval	Section 4.2.8	Critical for subambient sample collection, operational for pressurized sample collection
<b>GC/MS Analysis</b>				
Instrument Blank (IB)	Analysis of swept carrier gas through the preconcentrator to demonstrate the instrument is sufficiently clean prior to analysis of ICAL or daily beginning CCV	Each target VOC's concentration < 3x MDL or 0.2 ppb, whichever is lower	Section 4.2.10.5.2.2	Operational
BFB Tune Check	50 ng injection of BFB for tune verification of MS detector analyzed prior to initial calibration and every 24 hours of analysis thereafter (for quadrupole MS only)	Must meet abundance criteria listed in Table 4.2-2	Section 4.2.10.5.1 TO-15 Section 10.4.2	Critical

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
GC/MS Multi-Point Initial Calibration (ICAL)	Analysis of a minimum of five calibration levels covering approximately 0.1 to 5 ppb  Initially and minimally every three months thereafter, following failed BFB tune check, failed CCV, or when changes to the instrument affect calibration response	Average RRF $\leq$ 30% RSD and each calibration level must be within $\pm$ 30% of nominal  For linear regression (with either a linear or quadratic fit), $r \geq 0.995$ and each calibration level must be within $\pm$ 30% of nominal	Section 4.2.10.5.2.2 TO-15 Section 10.5.5.1	Critical
Secondary Source Calibration Verification (SSCV)	Analysis of a secondary source standard at the mid-range of the calibration curve to verify ICAL accuracy immediately after each ICAL	Recovery within $\pm$ 30% of nominal	Section 4.2.10.5.2.3	Critical
Continuing Calibration Verification (CCV)	Analysis of a known standard at the mid-range of the calibration curve to verify ongoing instrument calibration; following each daily BFB tune check and at the conclusion of each analytical sequence	Each target VOC must recover within 70-130% of the nominal spiked amount or the RRF must be within 30% of the mean ICAL RRF	Section 4.2.10.5.2.4 TO-15 Section 10.6.5	Critical
Internal Standards (IS)	Deuterated or non-naturally occurring compounds co-analyzed with all calibration standards, laboratory QC samples, and field-collected samples so as to monitor instrument response and assess matrix effects	Area response for each IS compound within $\pm$ 40% of the average response of the ICAL	Section 4.2.10.5.4 TO-15 Section 10.7.5	Critical
Preconcentrator Leak Check	Pressurizing or evacuating each canister connection to the preconcentrator to verify as leak-free prior to analysis	< 0.2 psi change/minute or manufacturer specifications	Section 4.2.10.5.2.1	Operational
Method Blank (MB)	Canister filled with clean humidified diluent gas (gas employed for dilution of standards and /or samples)  One with every analysis batch of 20 or fewer field-collected samples	Each target VOC's concentration < 3x MDL or 0.2 ppb, whichever is lower	Section 4.2.10.4.3 TO-15 Section 10.7.5	Operational
Laboratory Control Sample (LCS)	Canister spiked with known amount of target analyte at approximately the lower third of the calibration curve  <i>Recommended:</i> One with every analysis batch of 20 or fewer field-collected samples	Each target VOC's recovery must be 70 to 130% of its nominal spiked amount	Section 4.2.10.5.2.5	Operational
Retention Time (RT)	RT of each target compound and internal standard for all qualitatively identified compounds and internal standards	Each target VOC's RRT must be within $\pm$ 0.06 RRT units of its mean ICAL RRT  Each IS RT must be within $\pm$ 0.33 minutes of its mean ICAL RT	Sections 4.2.10.5.2.2 and 4.2.10.5.4 TO-15 Sections 10.5.5.2, 10.5.5.3, and 10.5.5.4	Critical

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Compound Identification	Qualitative identification of each target VOC in each standard, blank, QC sample, and field-collected sample (including field QC samples)	Signal-to-noise $\geq 3:1$  RT within prescribed window  Ion abundances of at least one qualifier ion within 30% of ICAL mean  Peak apexes co-maximized (within one scan for quadrupole MS) for quantitation and qualifier ions	Section 4.2.10.5.3	Critical
Replicate Analysis	A single additional analysis of a field-collected canister  Once with every analysis sequence (as prescribed in workplan)	Precision $\leq 25\%$ RPD for target VOCs with concentrations $\geq 5\times$ MDL	Section 4.2.10.5.2.5 TO-15 Section 11.1.1	Operational
Duplicate Sample	Field sample collected through the same inlet probe as the primary sample  10% of primary samples for sites performing duplicate sample collection (as prescribed in workplan)	Precision $\leq 25\%$ RPD of primary sample for concentrations $\geq 5\times$ MDL	Sections 4.2.4; 4.2.4.1	Operational
Collocated Sample	Field sample collected through a separate inlet probe as the primary sample  10% of primary samples for sites performing duplicate sample collection (as prescribed in workplan)	Precision $\leq 25\%$ RPD of primary sample for concentrations $\geq 5\times$ MDL	Sections 4.2.4 and 4.2.4.1	Operational

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
<i>Laboratory Readiness and Proficiency</i>				
Method Detection Limit	Determined initially and minimally annually thereafter and when method changes alter instrument sensitivity	MDL determined via 4.1 must be: Acrolein $\leq 0.09 \mu\text{g}/\text{m}^3$ Benzene $\leq 0.13 \mu\text{g}/\text{m}^3$ 1,3-Butadiene $\leq 0.10 \mu\text{g}/\text{m}^3$ Carbon Tetrachloride $\leq 0.017 \mu\text{g}/\text{m}^3$ Chloroform $\leq 0.50 \mu\text{g}/\text{m}^3$ Tetrachloroethylene $\leq 0.17 \mu\text{g}/\text{m}^3$ Trichloroethylene $\leq 0.20 \mu\text{g}/\text{m}^3$ Vinyl Chloride $\leq 0.11 \mu\text{g}/\text{m}^3$  These MDL MQOs current as of October 2015. Refer to current workplan template for up-to-date MQOs.	Sections 4.1 and 4.2.7	MQO
Stock Standard Gases	Purchased stock standard gases for each target VOC  All standards	Certified and accompanied by certificate of analysis  Recertified or replaced annually unless a longer expiration is specified by the supplier	Section 4.2.10.3.1	Critical
Proficiency Testing	Blind sample submitted to each laboratory to evaluate laboratory bias  Two per calendar year <sup>1</sup>	Each target compound within $\pm 25\%$ of the assigned target value  Failure of one PT must prompt corrective action. Failure of two consecutive PTs (for a specific core analyte) must prompt qualification of the analyte in field collected samples until return to conformance.	Section 2.1.4.1	Operational and MQO
<i>Canister and Sampling Unit Testing and Maintenance</i>				
Canister Leak Test	Testing of the leak tightness of each canister in the agency fleet  Annually, may be performed simultaneously with canister zero air check	Leak rate must be $\leq 0.1 \text{ psi/day}$	Section 4.2.6.1.1.1	Operational

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Canister Zero Check	Verification that a canister does not contribute to positive bias over an approximate 30-day period  <i>Strongly Recommended:</i> Each canister in the agency fleet once annually (or as defined by agency policy) or after major maintenance such as replacement of valve	All Tier I core target compounds must be < 0.2 ppb or < 3x MDL, whichever is lower	Section 4.2.6.1.1.1 TO-15 Section 8.4.3	Operational
Canister Known Standard Gas Check	Verification that a canister does not contribute to bias over an approximate 30-day period  <i>Strongly Recommended:</i> Each canister in the agency fleet once annually (or as defined by agency policy) or after major maintenance such as replacement of valve	All Tier I core target compounds must be within $\pm 30\%$ of nominal	Section 4.2.6.1.1.2	Operational
Sampling Unit Flow Calibration	Calibration of sampling unit flow controller  Initially and when calibration checks demonstrate flows are out of tolerance, or when components affecting flow are adjusted or replaced	Flow set to match the certified flow primary or transfer standard	Table 3.3-1 TO-15 Section 8.3.5	Practical
Sampling Unit Non-biasing Certification	Verification that the sampling unit does not contribute to bias  Prior to field deployment and annually thereafter, or when flow path components are repaired or replaced  Sampling units must be subject to a Zero Check and Known Standard Challenge	Zero Check – All Tier I core target analytes < 0.2 ppb or < 3x MDL, whichever is lower  Known Standard Challenge – All Tier I core target analytes within $\pm 15\%$ of the reference sample	Section 4.2.5.5	Operational
Sampling Unit Flow Calibration Check or Audit	Verification of sampling unit flow rate  Minimally quarterly, monthly recommended	Flow within $\pm 10\%$ of certified primary or transfer standard flow and design flow	Table 3.3-1	Practical
<b>Site Specifications and Maintenance</b>				
Sampling Unit Siting	Verify conformance to requirements  Annually	270° unobstructed probe inlet Inlet 2-15 meters above-ground level  $\geq 10$ meters from drip line of nearest tree  Collocated sampling inlets spaced within 4 meters of primary sampling unit inlet	Section 2.4	Operational

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category
Sample Probe and Inlet	Sample probe and inlet materials composition Annually	Chromatographic grade stainless steel or borosilicate glass	Section 4.2.3.2	Operational
Sample Inlet Filter	Particulate filter maintenance Minimally annually	Clean or replace the 2-µm sintered stainless steel filter	Section 4.2.3.3 TO-15 Section 7.1.1.5	Operational
Sampling Inlet and Inlet Line Cleaning	Sample inlet and inlet line cleaning or replacement Minimally annually - More often in areas with high airborne particulate levels	Cleaned with distilled water or replaced	Section 4.2.3.1	Operational
<b>Data Reporting</b>				
Data Reporting to AQS	Reporting of all results a given calendar quarter Quarterly, within 180 days of end of calendar quarter	All field-collected sample concentrations reported including data less than MDL. Field QC sample and laboratory replicates must also be reported (as required by workplan).	Section 3.3.1.3.15	Operational
AQS Reporting Units	Units must be as specified with each submission to AQS	ppbv	Section 3.3.1.3.15	Critical
Data Completeness	Valid samples compared to scheduled samples Annually	≥ 85% of scheduled samples	Section 3.2	MQO